Remarks/Arguments:

In the specification, the paragraph [0029] has been amended to clarify that each layer of the coating has the same composition, and that the agglomerate feed composition does not vary between successive passes during the deposition process. This is supported by paragraph [0010] which states that "titania coatings are prepared by thermal spray coating ultrafine titania agglomerates." It is further supported by original paragraph [0029] which states, "numerous deposition passes of the impinging particles are normally required to build up the coating **E**." The specification does not teach the use of a different composition for successive layers of the titania coating. It is not new matter to make explicit that which is implicit. Thus, the amendment to the specification adds no new matter.

By this amendment claim 17 is cancelled, claims 12, 25, and 26 are amended, claims 36-44 are added, and claims 12-20, 25, 26, and 28-44 are pending. Claims 12-16, 18-20, 25, 26 and 28-36 currently stand rejected. Specifically, claims 12-16, 18-20, 25, 26 and 28-36 are rejected under 35 U.S.C. §112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the Applicant regards as the invention. Claims 12-16, 18-20 and 28-36 are rejected under 35 U.S.C. §103(a) as being unpatentable over Hong (U.S. Pat. No. 5,545,337, hereinafter '337). Claims 25 and 26 are rejected as being unclear as to the relationship between "ultraparticles"

and the claimed subject matter. In response to the present Office Action, the applicant has amended claims 12, 25, and 26 and added claims 37-44. Following the arguments advanced in this office action, it is believed that the present amendments to the claims generally conforms the application to overcome the rejections. The applicant respectfully requests that the examiner reconsider and reexamine this application in view of the claim amendments made above and the following remarks.

The amendments to claims 12, 25 and 26 are supported in the specification. With respect to claim 12, at paragraph [0014] the specification states, "the titania preferably has a grain size of less than 500 nm." With respect to claims 25 and 26, at paragraph [0012] the specification states the invention provides "an ultrafine, preferably nanostructured titania coating bonded directly on a substrate of titanium."

New claims 37-44 are supported in the specification. With respect to claims 37 and 42, at paragraph [0029] the specification states "the coating **E** has a generally uniform composition." With respect to claims 38, 39, and 42, at paragraph [0012] the specification states, "an ultrafine, preferably nanostructured titania coating bonded directly on a substrate of titanium." With respect to claims 40-44, at paragraph [0026] the specification states, "the surface of the titanium substrate is preferably pretreated for deposition of the nanostructured titania by

precision roughening to 2-3 mils." Thus, in adding these claims, no new matter has been added.

Rejections Under 35 U.S.C. §112, second paragraph

Claims 12-16, 18-20, 25, 26, 28-36 currently stand rejected under 35 U.S.C. §112, second paragraph as being indefinite for failing to particularly point out and distinctly claim the subject matter which the Applicant regards as the invention. Applicant has considered the rejections in view of the Office Action and respectfully submits that the present claims are not indefinite and are thus allowable.

With respect to claim 12 and all claims dependent upon claim 12, the Office Action states that the location of the titania coating is unclear, specifically whether the coating is on the ball, the seat or on the substrate. The titania coating is on the titanium substrate which makes up the ball and seat of the valve. Support is found at paragraph [0012] of the specification, disclosing a "nanostructured titania coating bonded directly on a substrate of titanium." Further support is found at [0014] of the specification where it states "the ball and seat each comprise a titanium substrate and an ultrafine, preferably nanostructured titania coating." One skilled in the art can readily appreciate that the ball valve assembly comprises a titanium substrate and that the ball and seat of the valve have a titania coating bonded to the titanium substrate. The description in claim 12 is not unclear, is

defined within the specification, and is therefore allowable. Similarly, dependent claims 13-16, 18-20, 25-26, 28-36 rejected on the basis of their dependency on claim 12 are also allowable.

Referring to claims 25 and 26, which are rejected for lack of antecedent basis for the term "ultrafine particles." The Applicant has amended claims 25 and 26 to overcome this rejection. The amendment is supported at paragraph [0012] which states, the invention provides "an ultrafine, preferably nanostructured titania coating bonded directly on a substrate of titanium." The Applicant believes the claims, as amended, do not lack antecedent basis and are thus allowable.

Referring now to claims 28 and 29, to which clarification is requested. The Office Action states that particles are known to have "grain size", but questions whether a coating can have a grain size as well. Grain sizes in coatings are well known within the art and can be evaluated using a variety of methods, including but not limited to, X-Ray Diffraction, Transmission Electron Microscopy, and Scanning Electron Microscopy. The abstracts of several papers in which the evaluation of grain sizes in coatings is discussed are appended hereto. Grain sizes in coatings are commonly measured, and thus claims 28 and 29 are allowable.

Rejection Under 35 U.S.C. §103(a)

Claims 12-20, and 28-36 are rejected under 35 U.S.C. §103(a) as unpatentable over Hong (5,545,337). Hong discloses a composite comprising a titanium-based

substrate whose surface can be made resistant to corrosion by coating with titania. Hong further discloses the use of the composite in the construction of valve parts. To maintain a prima facie case of obviousness under 35 U.S.C. §103(a), the Examiner must show motivation, reasonable expectation of success, and that the prior art references teach or suggest all of the claim limitations. MPEP 706.02(j). The Office Action fails to cite a combination of references that teaches all the elements of claims 12-16, 18-20, and 28-49 as amended. Claims 12-16, 18-20, and 28-49 are improperly rejected, and therefore allowable.

With respect to claim 12, Hong fails to teach all elements of the claim. The Office Action suggests that Hong '337 teaches a method for the deposition of a titania coating on a titanium substrate. However, Hong does not teach a method for depositing a coating wherein the coating has a grain size of less than 500 nm, nor does Hong address the grain size of coatings at all. Furthermore, coatings having a grain size of less than 500 nm are not possible according to the method employed by Hong. Hong used Metco 102 titania powder supplied by Sulzer-Metco which is stated as having a particle diameter of approximately 50 microns. (See Hong '337, col. 7, lines 14-16). In order to obtain the nanostructured coatings described within the present application it is necessary to use ultrafine titania particles for the starting material, where ultrafine is defined as those having a diameter of less than 300 nm. This is supported in the specification. At paragraph [0007], the term "ultrafine" is

used to define materials having physical features less than 300 nm, and Examples 4, 5, and 7, at paragraphs [0037], [0038], and [0040], employ micron sized particles of TiO2 milled down to less than 300 nm. The 50,000 nm Hong particles cannot possibly grow to the smaller grain size in Applicant's invention, or completely melt, nucleate and quench to form such a fine grain size using their thermal spray approach. Furthermore, the Metco No. 102 titania powder is fused and lacks ultrafine grain structure.

The nanostructured coatings have enhanced properties representing a significant improvement over the prior art. Most importantly, the abrasion resistance of the ball valve seats of the present invention provide significantly improved performance and longevity in corrosive and erosive service applications compared to ball valves with seals made of the Hong-type materials. In Example 1 at paragraph [0035] an astonishing *three-fold* improvement in abrasion resistance was observed. Hong specifically states that the samples of titania on titanium produced using the methods given in the '337 patent have cracks. (See Hong, col. 11, lines 9-18). Furthermore, Hong speculates that the cracks penetrate to the base metal and that at operating temperatures, the cracks are likely to be larger than they appear at room temperature. (See Hong, col. 11, lines 16-18.)

Hong does not directly deposit titania on the titanium surface as the pending application does. Hong teaches that the composites are "graded," a well known

technique employed to decrease the likelihood of delamination at high temperature. (See Hong, col. 5, lines 50-52). As is stated in Hong, the coefficients of thermal expansion (CTEs) of titanium metal, and titanium dioxide, are sufficiently different that heating the titania coated titanium substrate of may lead to delamination of the material. (See Hong, col. 5, lines 52-61). To combat delamination, Hong teaches the deposition of multiple layers in admixtures with varying compositions of metal in order to mitigate the thermal expansion coefficient differences between adjacent layers. (See Hong, col. 5, lines 62-67). The mixed layers of ceramic (TiO2) and metal (Ti) are referred to as "cement." The present invention does not require the use of grading to prevent delamination of the titania layers at high temperature. The present invention does not depend on the use of a graded layer as titania can be uniformly deposited onto the titanium substrate or component, and no delamination of the titania layer is noted. See claims 37 and 42, and paragraph [0029].

Similarly, Hong teaches the use a metallic "bond coat" to provide a layer suitable for the titania to adhere to the base metal. (See Hong, col. 6, lines 3-9). Hong states that the bond coat is necessary to provide the titanium base metal with a rough surface conducive to good adhesion of the subsequently deposited cement. (See Hong, col. 6, lines 6-9). The present invention does not depend on such a coat, instead spraying the titania directly on the titanium substrate. See claims 38, 39 and 42, and paragraphs [0012] and [0024]. In the present invention, the surface can be

prepared by precision roughening to 2-3 mils. See claims 40-44 and paragraph [0026]. The roughening "can be achieved by impacting the substrate surface with Al2O3 or other abrasive particles using conventional sand blasting equipment, followed by cleaning the surface with solvent and a brush to remove as many of the residual abrasive particles as possible." See paragraph [0026]. Thus, Hong adds an additional layer, the "bond coat" to improve adhesion, while the present method can treat the existing base metal.

The foregoing amendments place the case in condition for allowance, raise no new issues and present no new matter. Accordingly, Applicant respectfully requests further examination of the application, as amended, reconsideration of the rejections, and allowance of the application.

The Commissioner is authorized to charge any fees associated with this communication to deposit account 501285. If the Examiner has any questions or comments regarding this communication, the undersigned can be contacted to expedite the resolution of this application.

Respectfully submitted,

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APPLICATION NOTE

GRAIN SIZE

Grain Size Analysis of Metallurgical Coatings Using FIB

Various aspects of grains such as size, uniformity and shape influence the performance of metallurgical coatings e.g. conductivity, appearance, adhesion and susceptibility to corrosion. A number of industries that would benefit from this technique include aerospace, biomedical, automotive, food packaging, and integrated circuits.

The characterization and testing of metallurgical coatings is a necessary step in the production process. The behavior of coatings under various test conditions needs to be evaluated to prevent failure of components in which these coatings are incorporated. Proper characterization provides a range of optimal operating conditions. Characterization of grain size in metallurgical coatings is an essential part of this effort.

The FIB (Focused Ion Beam) was used to obtain grain size information from an Al film. Figure 1 shows an image of the film's grains obtained by combining several images from the ion beam of the FIB. The ion beam was chosen to take advantage of the very high grain contrast obtained when imaging with ions. From this image, the grain boundaries are delineated using standard image processing techniques, the results of which are shown in Figure 2. The grain size can then be characterized using a number of methods, including intercept and grain area. Figure 3 is the result of color coding the grains according to ASTM grain size. A histogram showing the distribution of ASTM grain size for this sample is demonstrated in Figure 4.

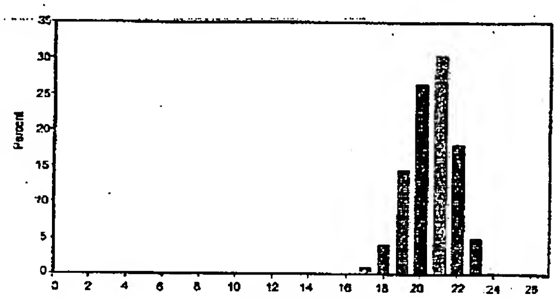

Figure 4

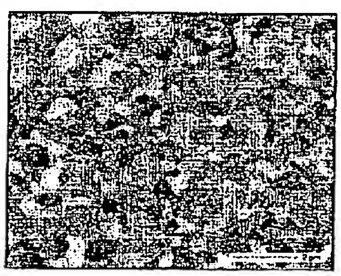

Figure 1

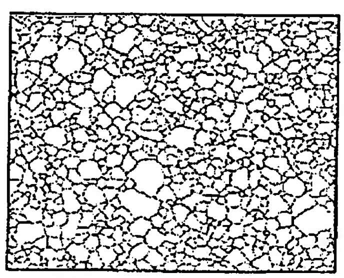

Figure 2

Figure 3

EAG Network
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EVANS PHI
Phone: 952-828-8411
EVANS EAST
Phone: 609-371-4800
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EVANS EUROPA
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More information is available on the EAGLABS® website at WWW.EAGLABS.COM

Industry: Metallurgical Coatings, Grain Size Analysis, Feature Analysis, ASTM
Technique: FIB, SEM

AN-MetCoat-345 6/02

Found at www.cea.com/literature/an-metcoat-345.pdf

Nano '02 Brno 2002

NANOCRYSTALLINE AND NANOCOMPOSITE COBALT-CHROMIUM COATINGS

RUDOLF NOVÁK, ZUZANA BUDINSKÁ, TOMÁŠ KUBART, TOMÁŠ POLCAR

CoCr and CoCrN coatings were sputtered on three types of substrates – glass, polished silicium and polished HSS. The aim of this work was to obtain nanostructured coatings and to evaluate their mechanical properties.

The deposition was carried out by means of an unbalanced magnetron with pulsed d.c. supply. The CoCr coatings were sputtered in argon, pressure 0,3 Pa, from an alloyed target CoCr 66/34 wt %. The substrate temperature was varied in the range from 50 ^{0}C to 620 ^{0}C, the substrate bias was varied in the range from –3 V to –150 V. Coatings thickness was in the range 2 – 5 microns. The coatings structures were studied by means of XRD, thickness was measured with Kalotest, microhardness with Hanemann hardness tester and tribological properties with the high temperature tribometer CSM.

The evaluation of XRD measurements showed that CoCr coatings had a deformed structure with (330) or (202) texture and grain size less than 40 nm. For substrate temperature over 550 ^{0}C the grain size rapidly increased. The microhardness is dependent on the deposition parameters, the highest value was about 7 GPa. It was achieved in the case of coatings deposited at the highest bias value, i.e. at –150 V. At elevated substrate temperatures the microhardness decreased a bit. The substrate choice influenced the internal stress: in coatings deposited on glass and steel was tensile stress, in coatings on silicium was compressive stress. All coatings properties showed that its structure agreed with the zone I in the zone structure model of thin films.

The CoCrN coatings were sputtered in Ar + N_2, total pressure 0,3 Pa, nitrogen partial pressure in the range 0,3 – 0,1 Pa. The XRD measurements showed that the structure deformation was increased in comparison with CoCr and the coating structure was Co – CrN, i.e. the coatings was a nanocomposite of CrN grains in Co matrix. At higher nitrogen pressure the grain size decreased in the range 10 – 6 nm and coating microhardness increased, the highest value was 35 GPa. At elevated substrate temperature the grain size decreased a little. The substrate bias did not influence the grain size and microhardness significantly. The internal stress was not effected with nitrogen partial pressure, but important was the substrate temperature. In coatings deposited at highest temperatures (more than 500 ^{0}C) there was relatively high compressive stress about 1 GPa. All coatings properties showed that its structure agreed with the zone T in the zone structure model of thin films.

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Found at http://csmt.fme.vutb.cz/nano02/abstract/31911732.pdf

ELECTRODEPOSITION OF NANOCRYSTALLINE ZINC

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ABSTRACT

Nanocrystalline materials exhibit properties that are fundamentally different from, and often superior to, those of the conventional polycrystalline counterparts. Zinc has been the most widely used electrodeposit for protection of steel against corrosion. Surface morphology, preferred orientation, and grain size have a significant effect on the mechanical properties of zinc electrodeposits. The role of surface morphology and preferred orientation on mechanical properties of zinc electrodeposits remains unclear [1]. However, it has been known that almost all of the mechanical properties can be effectively improved by refining the grain size. This is one reason nanocrystalline materials have recently received considerable attention [2]. Accordingly, many efforts have been made by researchers in order to refine the grain size of zinc coatings and improve their properties [3]. So far, the grain size of the electrodeposited zinc coatings is in the micrometer or sub-micrometer range. Therefore, the main goal of this work is to produce nanocrystalline (nc) zinc coatings and characterize their mechanical properties according to their grain size, surface morphology, and preferred orientation.

Electrodeposition is used to produce nc zinc coatings. The effect of additives and current waveform on the grain size and surface morphology of zinc deposits is studied by SEM, FESEM, and AFM. The preferred orientation of zinc deposits is studied by x-ray diffraction. Also, microhardness of the deposits is measured by a Knoop microhardness tester. We report the results of these studies and discuss their implications.

ACKNOWLEDGMENT

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